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Application Date: Oct. 21, 1937. No. 28772/37.

504,125

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Complete Specification Accepted: April 20, 1939.

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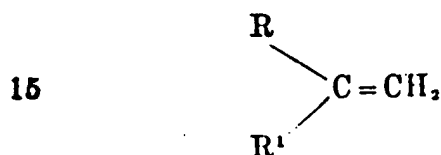
18. Mai 1939

PROVISIONAL SPECIFICATION

Process for the Manufacture of Aldehydes

I, ARTHUR CARPMAEL, British subject, of 24, Southampton Buildings, London, W.C.2, do hereby declare the nature of this invention (which has been communicated to me by I. G. Farbenindustrie Aktiengesellschaft, a joint stock company organised under the laws of Germany, of Frankfurt-on-Main, Germany), to be as follows:—

- 10 This invention relates to the manufacture of commercially valuable aldehydes. The process of manufacture according to the invention consists in that olefines of the general formula:



- 15 in which R indicates a hydrogen atom or an aliphatic, aromatic, fatty aromatic, alicyclic or heterocyclic residue or substituted residues of the specified type and R¹ a ring-system which is of aromatic nature or contains at least one unsaturated bond in conjugation with the ethylene bond, are caused to react in the presence of acid condensing agents containing chlorine, in particular of phosphorus oxychloride, with formylated secondary amines, advantageously formylmethylaniline.

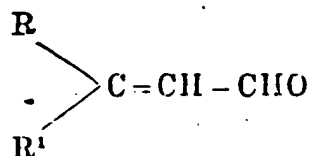
- 20 Among the olefines of the above specified type may be mentioned for example, styrene, 4-methoxystyrene, 4-dimethylaminostyrene, *o,o*-diphenylethylene, *o,o*-di-(4-chlorophenyl)-ethylene, *o,o*-di-(4-hydroxyphenyl)-ethylene, *o*-(4-hydroxyphenyl)-*o*-phenyl-ethylene, *o,o*-di-(1-naphthyl)-ethylene, *o,o*-di-(1-ethoxynaphthyl-4)-ethylene, *o,o*-bis-(*N*-diethyl-4-aminophenyl)-ethylene, *o,o*-bis-(*N*-dimethyl-4-aminophenyl)-ethylene, *o*-(1-methyl-2-phenyl)-indolyl-3-ethylene, *o*-(4-chlorophenyl)-*o*-(1-methyl-2-phenyl)-indolyl-3-ethylene, *o,o*-di-(1-methyl-2-phenyl)-indolyl-3,3'-ethylene, *o*-methylstyrene, and *o*-naphthylstyrene.

Particularly good results are obtained

[Price 1/-]

when phosphorus oxychloride and formylmethylaniline are employed in excess. The reaction can be carried out without solvents or also with the application of solvents which do not take part in the reaction, as for example aromatic hydrocarbons, halogen substitution products of aliphatic or aromatic hydrocarbons, nitrobenzene and the like.

The aldehydes produced of the general formula:



are suitable in particular as intermediate products for the manufacture of dyestuffs.

The following examples illustrate the invention:

EXAMPLE 1.

Into 150 parts by weight of phosphorus oxychloride are introduced drop by drop 100 parts by weight of formylmethylaniline at room temperature with stirring. After 2 hours stirring there are allowed to run into this mixture 52 parts by weight of styrene, during which operation the temperature should not exceed 25° C. and the reaction mixture is further stirred briskly for 24 hours. For destruction of the excess phosphorus oxychloride the reaction mass is poured on ice. It is treated with caustic soda-lye to an alkaline reaction and the methyl aniline and also the cinnamic aldehyde produced blown off with steam. From the distillate the mixture of the oils is extracted with ether or another suitable solvent, the ether shaken with 10% hydrochloric acid for removal of the methyl aniline, washed neutral and after drying over sodium sulphate evaporated. The cinnamic aldehyde formed distils at 125—130° C. under 18 mm.

EXAMPLE 2.

To a mixture produced according to example 1 of 150 parts by weight of phosphorus oxychloride and 100 parts by weight of formylmethylaniline are slowly

HA

added drop by drop with brisk stirring 67 parts by weight of 4-methoxystyrene, the temperature being maintained below 30° C. After 24 hours stirring the reaction mixture is poured on ice, rendered alkaline with caustic soda lye and the methyl aniline formed blown off with steam. In the distillation residue remains the 4-methoxycinnamic aldehyde as an oil which is separated from the aqueous alkaline solution by extraction with ether. After drying and evaporation the residue is distilled. The majority of the 4-methoxycinnamic aldehyde passes over between 165 and 175° C. under 18 mm. A small portion of the aldehyde can also be isolated from the methyl aniline driven off with steam.

In the same manner as 4-methoxycinnamic aldehyde is produced from 4-methoxystyrene, 4-(N - dimethyl)-amino-cinnamic aldehyde can be obtained from 4-dimethylaminostyrene.

EXAMPLE 3.

Into the mixture produced according to example 1 of 150 parts by weight of phosphorus oxychloride and 100 parts by weight of formylmethylaniline are slowly introduced drop by drop at 25° C. with good stirring 80 parts by weight of α,α -diphenylethylene and stirring is continued for about 24 hours. The excess of phosphorus oxychloride is then destroyed by pouring the reaction mixture on ice, the mixture is rendered alkaline with caustic soda lye and the methyl aniline formed removed with steam. The oily residue is separated from the aqueous-alkaline solution by taking up in benzene. After drying the benzene solution and evaporating the solvent the remaining oil is distilled. The β,β -diphenyl-acrolein formed passes over at 195—200° C. under 19 mm as an oil which gradually solidifies.

In an analogous manner the α,α -di-(4-chlorophenyl)-acrolein is obtained from the corresponding ethylene by reaction with formylmethylaniline and phosphorus oxychloride. (The ethylene is obtained from 4,4'-dichlorobenzophenone and methyl magnesium bromide by splitting off of water from the 4,4'-dichlorodiphenyl methylcarbinol first formed.)

EXAMPLE 4.

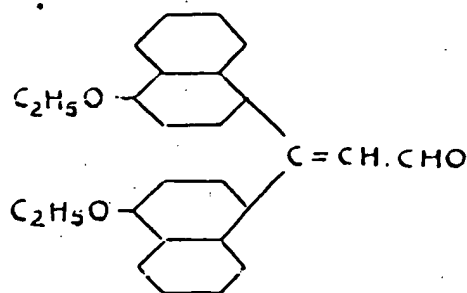
Into a mixture of 150 parts by weight of phosphorus oxychloride and 100 parts by weight of formylmethylaniline are introduced in small portions at 20—25° C. 90 parts by weight of α,α -di-(4-hydroxyphenyl)-ethylene with stirring. After 20 hours the mixture is poured on ice, treated with concentrated caustic soda lye to an alkaline reaction and subjected to steam distillation. After driv-

ing off the methylaniline the β,β -di-(4-hydroxyphenyl)-acrolein is precipitated with concentrated hydrochloric acid. It is taken up in benzene and remains after evaporation of the benzene as a crystalline residue.

In the same manner also from the 4-hydroxydiphenylethylene and from the mono- and diethers of the hydroxydiphenyl ethylenes the corresponding acroleins can be produced very smoothly and in good yields.

EXAMPLE 5.

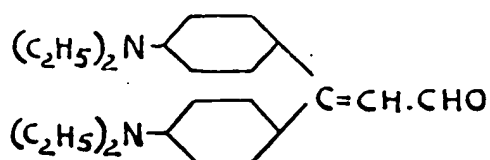
To 200 parts by weight of phosphorus oxychloride are added drop by drop slowly at room temperature 100 parts by weight of formylmethylaniline and into the mixture thus produced after 2 hours stirring 100 parts by weight of α,α -di-(1-ethoxy-naphthyl-4)-ethylene are introduced, the temperature being maintained at about 25° C. After 15 hours stirring the reaction mixture is poured on ice, rendered alkaline with caustic soda lye and the methylaniline formed distilled off with steam. The solid residue formed on cooling is filtered off and the β,β -di-(1-ethoxynaphthyl-4) - acrolein obtained pure by recrystallisation from ligroin. It possesses the following structure:



EXAMPLE 6.

Into a mixture of 150 parts by weight of phosphorus oxychloride and 80 parts by weight of formylmethylaniline, obtained as described in example 1 are introduced in small portions 100 parts by weight of α,α -4,4'-tetraethyl-diaminodiphenylethylene, the temperature not being allowed to exceed 30° C. The reaction mixture is stirred for 12 hours longer, poured on ice and rendered alkaline with caustic soda lye. Thereupon the oil which floats on the surface of the lye is separated from the aqueous layer, taken up in a mixture of 200 parts by weight of alcohol and 50 parts by weight of concentrated caustic soda lye and the solution is stirred for 3 hours at 80° C., whereupon it is treated with 500 parts of water and the alcohol together with methylaniline formed blown off with steam. The residue is taken up in benzene, the benzene solution dried over

sodium sulphate and the benzene evaporated. The remaining β,β -bis-(N-diethyl-4-aminophenyl)-acrolein of the formula:

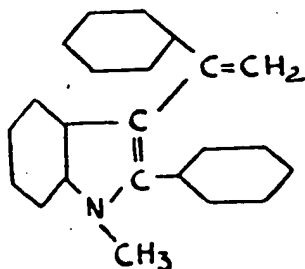


5 can be obtained pure by recrystallisation from aqueous alcohol.

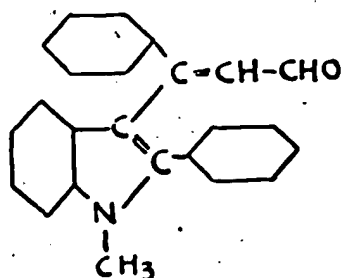
In a corresponding manner the β -(N-dimethyl-4-aminophenyl)- β -phenyl-acrolein and also the β,β -bis-(N-dimethyl-4-aminophenyl)-acrolein can be obtained in good yield from the corresponding ethylenes (which for their part can be produced from the corresponding benzophenones).

15 **EXAMPLE 7.**

100 parts by weight of α -phenyl- α -(1-methyl-2-phenyl)-indolyl-3-ethylene of the formula:



20 (which can be obtained from phenyl-(1-methyl-2-phenyl)-indolyl-3-ketone by reaction with methyl magnesium bromide) are introduced at 25° C. with stirring into a mixture obtained according to example 1
25 from 150 parts by weight of phosphorus oxychloride and 100 parts by weight of formylmethylaniline. The mixture is stirred for 12 hours, poured on ice, rendered alkaline with concentrated
30 caustic soda lye and freed with steam from the methylaniline formed. Soon after cooling there crystallises from the first oily residue the β -phenyl- β -(1-methyl-2-phenyl)-indolyl-3-acrolein of
35 the formula:

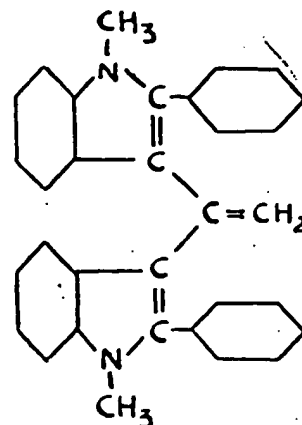


as a pale yellow powder.

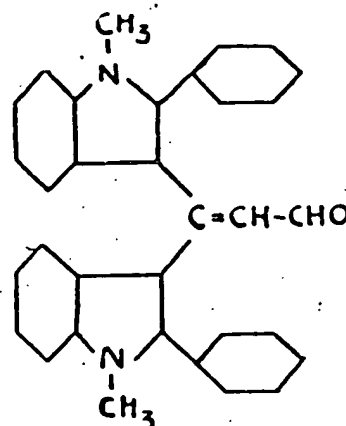
In a corresponding manner the β -(4-chlorophenyl)- β -(1-methyl-2-phenyl)-indolyl-3-acrolein is obtained from the 40 corresponding ethylene (which itself is produced from the corresponding ketone with methyl magnesium bromide).

EXAMPLE 8.

150 parts by weight of α,α -di-(1-45 methyl-2-phenyl)-indolyl-3,3'-ethylene of the formula:



(which is obtained from the corresponding ketone with methyl magnesium 50 bromide) are dissolved in the same quantity of phosphorus oxychloride and slowly introduced drop by drop into a mixture of 100 parts by weight of formylmethylaniline and 150 parts by 55 weight of phosphorus oxychloride. After 12 hours stirring at room temperature the mixture is poured on ice, rendered alkaline with caustic soda lye and freed from the methylaniline formed by steam distillation. After cooling there crystal- 60 lises from the distillation residue the β,β -(1-methyl-2-phenyl)-indolyl-3,3'-acrolein of the formula:



in light yellow scales.

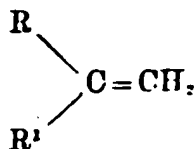
Dated the 21st day of October, 1937.
CARPMAELS & RANSFORD,
Agents for Applicant,
24, Southampton Buildings,
London, W.C.2.

COMPLETE SPECIFICATION

Process for the Manufacture of Aldehydes

I, ARTHUR CARPMAEL, British subject, of 24, Southampton Buildings, London, W.C.2, do hereby declare the nature of this invention (which has been communicated to me by I. G. Farbenindustrie Aktiengesellschaft, a joint stock company organised under the laws of Germany, of Frankfurt-on-Main, Germany), and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the manufacture of commercially valuable aldehydes. The process of manufacture according to the invention consists in that olefines of the general formula:



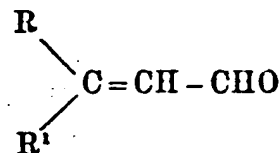
in which R indicates a hydrogen atom or an aliphatic, aromatic, fatty aromatic, alicyclic or heterocyclic residue or substituted residues of the specified type and R¹ a ring-system which is of aromatic nature or contains at least one unsaturated bond in conjugation with the ethylene bond, are caused to react in the presence of acid condensing agents containing chlorine, in particular of phosphorus oxychloride, with formylated secondary amines, advantageously formylmethylaniline.

Among the olefines of the above specified type may be mentioned for example, styrene, 4-methoxystyrene, 4-dimethylamino-styrene, *α,α*-diphenylethylene, *α,α*-di-(4-chlorophenyl)-ethylene, *α,α*-di-(4-hydroxyphenyl)-ethylene, *α*-(4-hydroxyphenyl)-*α*-phenyl-ethylene, *α,α*-di-(1-naphthyl)-ethylene, *α,α*-di-(1-ethoxy-naphthyl-4)-ethylene, *α,α*-bis-(*N*-diethyl-4-aminophenyl)-ethylene, *α*-(*N*-dimethyl-4-aminophenyl)-*α*-phenylethylene, *α,α*-bis-(*N*-dimethyl-4-aminophenyl)-ethylene, *α*-phenyl-*α*-(1-methyl-2-phenyl)-indolyl-3-ethylene, *α*-(4-chlorophenyl)-*α*-(1-methyl-2-phenyl)-indolyl-3-ethylene, *α,α*-di-(1-methyl-2-phenyl)-indolyl-3.3'-ethylene, *α*-methylstyrene, and *α*-phenyl-*α*-(1-naphthyl)-ethylene.

Particularly good results are obtained when phosphorus oxychloride and formylmethylaniline are employed in excess. The reaction can be carried out without solvents or also with the applica-

tion of solvents which do not take part in the reaction, as for example aromatic hydrocarbons, halogen substitution products of aliphatic or aromatic hydrocarbons, nitrobenzene and the like.

The aldehydes produced of the general formula:



are suitable in particular as intermediate products for the manufacture of dyestuffs.

The following examples illustrate the invention:

EXAMPLE 1.

Into 150 parts by weight of phosphorus oxychloride are introduced drop by drop 100 parts by weight of formylmethylaniline at room temperature with stirring. After two hours stirring there are allowed to run into this mixture 52 parts by weight of styrene, during which operation the temperature should not exceed 25° C. and the reaction mixture is further stirred briskly for twenty-four hours. For destruction of the excess phosphorus oxychloride the reaction mass is poured on ice. It is treated with caustic soda lye to an alkaline reaction and the methyl aniline and also the cinnamic aldehyde produced blown off with steam. From the distillate the mixture of the oils is extracted with ether or another suitable solvent, the ether shaken with 10% hydrochloric acid for removal of the methylaniline, washed neutral and after drying over sodium sulphate evaporated. The cinnamic aldehyde formed distils at 125–130° C. under 18 mm.

EXAMPLE 2.

To a mixture produced according to example 1 of 150 parts by weight of phosphorus oxychloride and 100 parts by weight of formylmethylaniline are slowly added drop by drop with brisk stirring 67 parts by weight of 4-methoxystyrene, the temperature being maintained below 30° C. After twentyfour hours stirring the reaction mixture is poured on ice, rendered alkaline with caustic soda lye and the methyl aniline formed blown off with steam. In the distillation residue remains the 4-methoxycinnamic aldehyde as an oil

which is separated from the aqueous alkaline solution by extraction with ether. After drying and evaporation the residue is distilled. The majority of the 4-methoxycinnamic aldehyde passes over between 165 and 175° C. under 18 mm. A small portion of the aldehyde can also be isolated from the methyl aniline driven off with steam.

In the same manner as 4-methoxycinnamic aldehyde is produced from 4-methoxystyrene, 4-(N-dimethyl-amino)cinnamic aldehyde can be obtained from 4-dimethylamino-styrene.

EXAMPLE 3.

Into the mixture produced according to example 1 of 150 parts by weight of phosphorus oxychloride and 100 parts by weight of formylmethylaniline are slowly introduced drop by drop at 25° C. with good stirring 80 parts by weight of α,α -diphenylethylene and stirring is continued for about twenty-four hours. The excess of phosphorus oxychloride is then destroyed by pouring the reaction mixture on ice, the mixture is rendered alkaline with caustic soda lye and the methyl aniline formed removed with steam. The oily residue is separated from the aqueous-alkaline solution by taking up in benzene. After drying the benzene solution and evaporating the solvent the remaining oil is distilled. The β,β -di-phenyl-acrolein formed passes over at 195–200° C. under 19 mm as an oil which gradually solidifies.

In an analogous manner the β,β -di-(4-chlorophenyl)-acrolein is obtained from the corresponding ethylene by reaction with formylmethylaniline and phosphorus oxychloride. (The ethylene is obtained from 4,4'-dichlorobenzophenone and methyl magnesium bromide by splitting off of water from the 4,4'-dichlorodiphenyl methylcarbinol first formed.)

EXAMPLE 4.

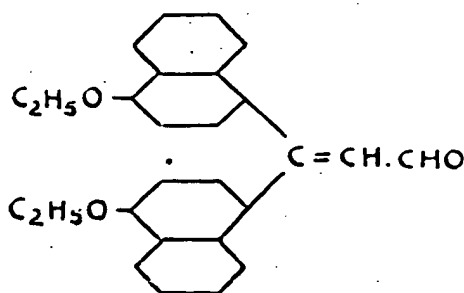
Into a mixture of 150 parts by weight of phosphorus oxychloride and 100 parts by weight of formylmethylaniline are introduced in small portions at 20–25° C. 90 parts by weight of α,α -(4-hydroxyphenyl)-ethylene with stirring. After twenty hours the mixture is poured on ice, treated with concentrated caustic soda lye to an alkaline reaction and subjected to steam distillation. After driving off the methylaniline the β,β -di-(4-hydroxyphenyl)-acrolein is precipitated with concentrated hydrochloric acid. It is taken up in benzene and remains after evaporation of the benzene as a crystalline residue.

In the same manner also from the α -phenyl-(p -hydroxyphenyl)-ethylene, the β -phenyl- β -(p -hydroxyphenyl)-acro-

lein and from the mono and diethers of the di-(hydroxyphenyl)-ethylene, the mono and diethers of the β,β -(p -hydroxyphenyl)-acrolein can be produced very smoothly and in good yields.

EXAMPLE 5.

To 200 parts by weight of phosphorus oxychloride are added drop by drop slowly at room temperature 100 parts by weight of formylmethylaniline and into the mixture thus produced after two hours stirring 100 parts by weight of α,α -di-(1-ethoxy-naphthyl-4)-ethylene are introduced, the temperature being maintained at about 25° C. After fifteen hours stirring the reaction mixture is poured on ice, rendered alkaline with caustic soda lye and the methylaniline formed distilled off with steam. The solid residue formed on cooling is filtered off and the β,β -di-(1-ethoxynaphthyl-4)-acrolein obtained pure by recrystallisation from ligroin. It possesses the following structure:

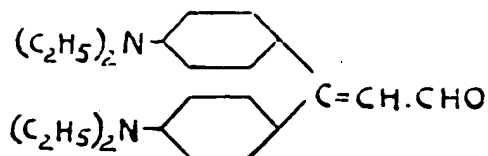


The diethoxynaphthylethylene is obtainable from diethoxynaphthylketone by treatment with methylmagnesium-bromide and splitting off of water from the originally formed diethoxynaphthyl-methylcarbinol. The ketone mentioned may be obtained by conversion of ethyl- α -naphthylether with phosgene in the presence of aluminiumchloride and an inert solvent.

EXAMPLE 6.

Into a mixture of 150 parts by weight of phosphorus oxychloride and 80 parts by weight of formylmethylaniline, obtained as described in example 1, are introduced in small portions 100 parts by weight of α,α -bis-(N-diethyl-4-aminophenyl)-ethylene, the temperature not being allowed to exceed 30° C. The reaction mixture is stirred for twelve hours longer, poured on ice and rendered alkaline with caustic soda lye. Thereupon the oil which floats on the surface of the lye is separated from the aqueous layer, taken up in a mixture of 200 parts by weight of alcohol and 50 parts by weight of concentrated caustic soda lye and the solution is stirred for three hours at 80° C., whereupon it is treated with 500 parts

of water and the alcohol together with methylaniline formed blown off with steam. The residue is taken up in benzene, the benzene solution dried over sodium sulphate and the benzene evaporated. The remaining β,β -bis-(N-diethyl-4-aminophenyl)-acrolein of the formula:

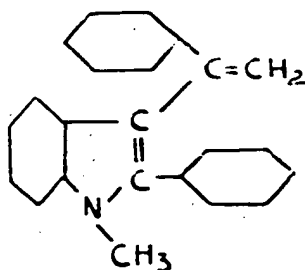


can be obtained pure by recrystallisation from aqueous alcohol.

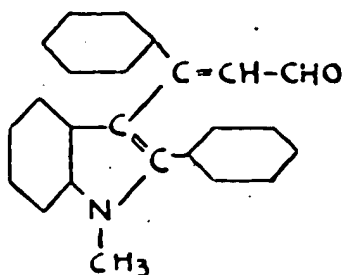
In a corresponding manner the β -(N-dimethyl-4-aminophenyl) - β - phenyl-acrolein and also the β,β -bis-(N-dimethyl-4-aminophenyl)-acrolein can be obtained in good yield from the corresponding ethylenes (which for their part can be produced from the corresponding benzophenones.)

EXAMPLE 7.

100 parts by weight of α -phenyl- α -(1-methyl-2-phenyl) - indolyl-3-ethylene of the formula:



(which can be obtained from phenyl-(1-methyl-2-phenyl)-indolyl-3-ketone by reaction with methyl magnesium bromide) are introduced at 25° C. with stirring into a mixture obtained according to example 1 from 150 parts by weight of phosphorus oxychloride and 100 parts by weight of formylmethylaniline. The mixture is stirred for twelve hours, poured on ice, rendered alkaline with concentrated caustic soda lye and freed with steam from the methylaniline formed. Soon after cooling there crystallises from the first oily residue the β -phenyl- β -(1-methyl-2-phenyl)-indolyl-3-acrolein of the formula:

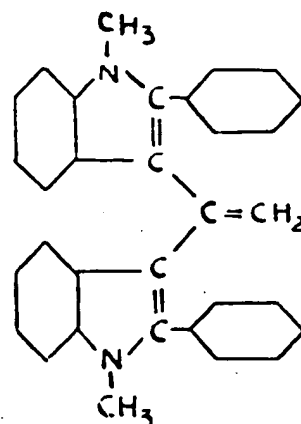


as a pale yellow powder.

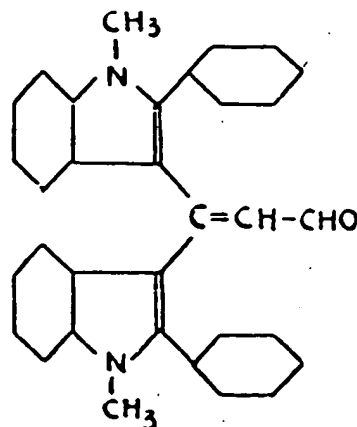
In a corresponding manner the β -(4-chlorophenyl)- β -(1-methyl-2-phenyl)-indolyl-3-acrolein is obtained from the corresponding ethylene (which itself is produced from the corresponding ketone with methyl magnesium bromide).

EXAMPLE 8.

150 parts by weight of α,α -di-(1-methyl-2-phenyl)-indolyl-3,3'-ethylene of the formula:



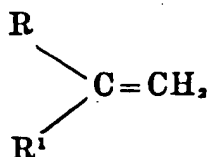
(which is obtained from the corresponding ketone with methyl magnesium bromide) are dissolved in the same quantity of phosphorus oxychloride and slowly introduced drop by drop into a mixture of 100 parts by weight of formylmethylaniline and 150 parts by weight of phosphorus oxychloride. After twelve hours stirring at room temperature the mixture is poured on ice, rendered alkaline with caustic soda lye and freed from the methylaniline formed by steam distillation. After cooling there crystallises from the distillation residue the di- β,β -(1-methyl-2-phenyl)-indolyl-3,3'-acrolein of the formula:



in light yellow scales.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. Process for the manufacture of aldehydes by the interaction of olefines of the general formula:



5 in which R indicates a hydrogen atom or an aliphatic, aromatic, fatty aromatic, alicyclic or heterocyclic residue or substituted residues of the specified type and R' a ring system which is of aromatic
10 nature or contains at least one unsaturated bond in conjugation with the

ethylene bond, in the presence of acid condensing agents containing chlorine, with formylated secondary amines.

2. Process for the manufacture of 15 aldehydes substantially as described in the examples.

3. Aldehydes whenever prepared or produced by the process claimed in either of claims 1 and 2 or by any process which 20 is an obvious chemical equivalent thereof.

Dated this 13th day of October, 1938.

CARPMAELS & RANSFORD.

Agents for Applicant,
24, Southampton Buildings,
London, W.C.2.